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The effect of diluent gases in the shock tube and rapid compression machine

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Studying the details of hydrocarbon chemistry in an internal combustion engine is not straightforward. A number of factors, including varying conditions of temperature and pressure, complex fluid motions, as well as variation in the composition of gasoline, render a meaningful characterization of the combusting system difficult. Some simplified experimental laboratory devices offer an alternative to complex engine environments: they remove some of the complexities that exist in real engines but retain the ability to work under engine-relevant conditions. The choice of simplified experimental devices is limited by the range of temperature and pressure at which they can operate; only the shock tube and rapid compression machine (RCM) can reach engine–relevant temperatures and pressures quickly enough and yet withstand the high pressures that occur after the ignition event. Both devices, however, suffer a common drawback: the use of inert diluent gases has been shown to affect the measured ignition delay time under some experimental conditions. Interestingly, this effect appears to be opposite in the shock tube and RCM: in the comparative study of the carrier gases argon and nitrogen, argon decreases the ignition delay time in the shock tube, but increases it in the RCM. This observation is investigated in more detail in this study.

1. Introduction

A key to improving the efficiency of internal combustion engines is an understanding of the chemistry that takes place when a fuel burns. A complete qualitative and quantitative characterization of these chemical reactions would allow us to predict the chemistry of fuel oxidation at a wide range of pressures and temperatures, leading to an increase in the efficiency and performance of combustion engines, and a reduction in harmful engine emissions.

However, studying the details of hydrocarbon chemistry in an internal combustion engine is not straightforward. Its environment is beset by widely varying conditions of temperature and pressure, combined with complex fluid motions [1–11]. In addition, the composition of gasoline is variable, and may contain in excess of 300 components [12]. All of these factors render a meaningful characterization of the combusting system difficult. The majority of engine studies use either a very limited set of pure compounds or a complex fuel mixture. It is virtually impossible to perform a systematic investigation of the combustion chemistry of a family of volatile compounds, such as the nine isomers of heptane, as these are either available in restrictively small quantities or are prohibitively expensive.

While it is evidently possible to collect good data from engine experiments, the numerical simulation of such results is not straightforward. Iida *et al.* [13] for instance employed pure *n*-

butane as surrogate fuel for gasoline and measured the concentrations of a wide range of compounds in the exhaust of a CFR engine operating in homogeneous charge compression ignition (HCCI) mode. Despite the availability of good detailed mechanisms for butane including important nitrogen chemistry [14], Iida *et al.* were unable to simulate their results successfully.

A chemically meaningful study of the combustion of even a pure compound in an engine environment would require the simultaneous description of the chemical reactions and complex flow environment: the resolution of hundreds or thousands of detailed chemical reactions and the 3–dimensional fluid flow interactions. Such a marriage is currently beyond scientific capability. Some simplified experimental laboratory devices offer an alternative to complex engine environments: they remove some of the complexities that exist in real engines but yet retain the ability to work under engine-relevant conditions. This allows the study of, for instance, a single fuel component or a particular specified gas-phase reaction at a detailed level, while facilitating relatively simple data collection and interpretation. The choice of simplified experimental devices is limited by the range of temperature and pressure at which they can operate; only the shock tube and rapid compression machine (RCM) can reach engine–relevant temperatures and pressures quickly enough and yet withstand the high pressures that occur after the ignition event. The shock tube is useful for the study of high temperature and pressure reactions, while intermediate and low temperature reactions can be studied at a wide range of pressures in a rapid compression machine. Both devices are valuable as they provide important data on ignition delay times of reactive gases, however, they both suffer a common drawback: the use of inert diluent gases has been shown to affect the measured ignition delay time under some experimental conditions. Interestingly, this effect appears to be opposite in the shock tube and RCM: in the comparative study of the carrier gases argon and nitrogen, argon decreases the ignition delay time, τ, in the shock tube, but increases it in the RCM. This observation is investigated in more detail in *this study.*

Shock tube:

In the shock tube the premixed test gas is heated by a shock wave in ~1 nanosecond to pre-selected temperature and pressures, and the progress of the reaction can be followed - safe in the knowledge that wall-catalyzed reactions do not contribute, since the observation time is short compared to diffusion timescales. The shock wave is usually generated by the rupturing of a diaphragm which separates two sections containing high – and low–pressures, respectively. The high–pressure section usually contains helium, and the fuel/oxygen/diluent mixture is contained in the low–pressure compartment. Generally, reflected shock temperature and pressure ranges in the shock tube are 1,000-3,000 K and 1-17 atm.

The time scale in shock tube is very short, typically 10-1,000 microseconds, which limits its use to the high temperature regime [15]. However, techniques to lengthen the test time do exist, such as the tailored interface in hypersonic-shock tunnels, first developed by Herzberg *et al.* [16], which eliminates reflected shock-contact surface interactions by matching the acoustic impedance across the contact surface. A more recent method by Amadio *et al.* [17] uses unconventional driver gas mixtures to slow down the rarefaction wave and thereby increase the test time somewhat. Despite these two approaches extending the experimental timescale somewhat, neither of them is fully satisfactory and cannot compete with the range of experimental conditions accessible in the RCM. Simulating the shock tube experiment is relatively straightforward because assumptions regarding the state of the test gas can be made

due to the short test time involved. For example, Chemkin's module SHOCK is based on the conservation equations for one-dimensional flow through an arbitrarily assigned area, transport processes and viscous effects are assumed negligible, the pressure is constant, and the flow is assumed adiabatic [18]. Shock tube experiments are generally carried out with a premixed mixture of fuel, oxygen and argon, since the shock wave behavior is optimized in monatomic carrier gases, such as argon. Dilute fuel mixtures which contain only small proportions of fuel and oxygen in more than 90% of argon are therefore studied under the most optimal shock wave conditions since the fraction of polyatomic gas is kept small.

In their recent study, 'Interpreting Shock Tube Ignition Data', Davidson *et al.* [19] evaluated shock tube ignition delay time data in terms of (i) type and (ii) quality for developing and validating combustion reaction mechanisms. Their study included an evaluation of the effect of diluent or bath gases on the ignition delay time, for an *iso*-octane/oxygen/diluent mixture using two kinetic mechanisms [20,21]. Davidson *et al.* reported that a different ignition delay time would be recorded if the diluent argon was replaced by nitrogen for a mixture containing 0.16% *iso*-octane, 2% oxygen and 97.84% diluent gas. They predicted an ignition delay time that was 9% longer when nitrogen was to be used, thus highlighting a dependency of the recorded ignition delay time with the diluent gas used. They attributed this difference to the effect of the heat capacity of the bulk carrier gas, which is related to the time scale of the vibrational relaxation of a diatomic carrier gas. This study elaborates on the findings reported by Davidson *et al.* and investigates in more detail the effect of the diluent gas under various experimental conditions in the shock tube.

RCM:

Rapid compression machines are best suited to replicate the environment of an internal combustion engine. There are about a dozen or so machines in operation in the world today. Analogous to the internal combustion engine, the RCM is a device that rapidly compresses a premixed fuel/oxygen/diluent gas mixture to pre-selected temperatures and pressure. It simulates only a single stroke of the combustion engine, and thus allows the study of auto-ignition under more favorable conditions than those present in a real engine. The compression ratio, initial charge composition, and temperature can be well controlled while contaminations of abraded metal particles or oil mist are eliminated. Provided that favorable conditions are reached at the end of the compression stroke, the fuel auto-ignites spontaneously after a characteristic delay time during which the fuel is pre-conditioned. Post-compression conditions of temperature and pressure are typically in the range 700–1,200 K and 1–6 MPa, and typical test times are in the region of 1–200 ms.

In order to minimize heat losses the compression process must be very rapid; however, too rapid a compression can lead to aerodynamic heating and requires high rates of deceleration and consequently over-robust engineering [2]. The information collected normally includes pressure and/or light emission as a function of time but unfortunately not temperature since it is not possible to measure temperature to the required accuracy within the short test time [4, 6, 22, 23]. Gas sampling provides a means of obtaining more meaningful qualitative and quantitative analytical data. It involves the rapid removal and quenching of a gas sample, before ignition has taken place, and its subsequent analysis. This allows the identification and quantitative analysis of stable intermediate species, and thus provides a better insight into the reaction pathways

during the pre-conditioning period. The method by which a sample is taken from the chamber varies; we have developed a fast-acting piezoelectric valve [24], while other groups have used a bursting disk [2, 25].

The RCM design is continuously developing; Donovan *et al.* [7] built and used a free-piston RCM, for example, to study the high temperature combustion characteristic typical in HCCI engines. This design is unique because it uses a purposely shaped sabot to compress the test gas, with the effect that only a small portion of the gas is confined to the test manifold, while the stirring vortex is trapped outside the test manifold. Fluid disturbances and unnecessary heat transfer are thereby minimized. A variant of the traditional RCM is the rapid compression expansion machine (RCEM): a high-pressure, free-piston machine, which was developed and used to investigate the auto-ignition behavior of a wide range of gaseous and liquid hydrocarbon fuels [26] and subsequently used to study the ignition temperatures and the rates and extent of combustion of *n*-heptane and air mixtures [27]. This device is unique because it uses a non-locking piston which is said to better approximate the dynamic behavior of a continuously moving internal combustion engine piston.

The RCM used in this study is a unique twin piston machine, which was originally used by Shell Thornton [2] and modified extensively since it was moved to Galway [28]. The advantage of this machine is the particular short compression time of 16 ms for a stroke of 336 mm (168mm per piston), and the plane of symmetry which facilitates minimal gas movement in the center of the reaction chamber. All experiments were performed with creviced piston heads, an idea that was first pioneered by Park and Keck [1] and further developed by Lee and Hochgreb [3]. Provided their optimal size and shape, piston head crevices effectively swallow the cooler boundary that is scraped from the chamber wall during the piston movement, thus preventing it from mixing with the hot compressed gas. The net effect is a more homogeneous distribution of temperature during the post-compression period. Since the rates of chemical reactions are extremely sensitive to temperature, non-homogeneous temperature fields render realistic kinetic modeling very difficult or even impossible.

The importance of an optimal piston head design was highlighted by Würmel and Simmie [9]. It was shown, by means of a computational fluid dynamic (CFD) study, that the crevice volume, its distance from the chamber and the ease with which the gas can flow into the crevice are crucial design considerations. It was determined that an optimal design depends strongly on the thermo-physical properties of the gas, where a piston head crevice that worked well for say pure nitrogen and argon was not sufficient when pure helium was tested. This of course has important implications when a fuel/oxygen/helium mixture with a high proportion of helium is studied.

Simulating the RCM:

The RCM chamber is a three-dimensional, potentially turbulent environment. An insight into the chemical reactions which eventually give rise to ignition can only be achieved by kinetic modeling of the hundreds or even thousands of chemical reactions within this complex environment, a task that is currently only possible for very simple fuels. Therefore, simulation of the chemical kinetics in the RCM are still flawed by oversimplifications, despite having been proven to be incorrect. For instance, multi-dimensional simulations do solve the complex flow environment but lack the correct representation of chemical kinetic detail; they are predominantly coupled to reduced models, which summarize the combustion process as a set of

global reactions [29]. Shi *et al.* [30] did make some progress by applying the commercial code Fluent to detailed chemical kinetics, however, they do stress that the use of full mechanisms even for methane in real CFD simulations is still computationally prohibited. In a previous study [8] the commercial software STAR/KINetcis was applied to simulate the combustion of hydrogen in our twin-piston RCM and reasonably good agreement with experimental measurements was achieved, however, computations took 5 days using a mechanism of 10 reactions and 19 species, making it prohibitive to progress to more complex fuels.

One-dimensional simulations, in contrast, do solve detailed chemistry. However these are often coupled to assumptions of homogeneous, adiabatic compressed gas conditions [31], which have been demonstrated to be incorrect [3,9,10]. In a recent study Mittal and Sung investigated aerodynamics affects in the RCM by applying PLIF measurements of acetone [10, 11]. They underpinned their experimental finding with a CFD study and confirmed that the adiabatic core theory does not hold for RCM experiments when flat piston heads are used. Mittal and Sung presented some experimental results, in which they had measured ignition delay times at similar compressed conditions of composition, temperature and pressure, performed with both flat and creviced piston heads. They showed that the flat piston experiment leads to a smaller post-compression drop in pressure and longer ignition delays than the creviced piston head case. Their explanation was brief:

> 'The combined effect of the lower core temperature than that calculated using the adiabatic core hypothesis and the higher post compression pressure for the flat piston case alters the ignition delay as depicted in Figure 19'.

We find these results unusual and counterintuitive, as the penetration of the cold boundary layer gas into the hot core, caused by the flat piston head, would be expected to reduce the core temperature and pressure, resulting in longer ignition delay times. We have shown in our CFD calculations that, provided a good design is used, the groove in the creviced piston head, will prevent the mixing of cold and hot gas, which should lead to a shorter ignition delay time, unless the post-compression condition fall into the negative temperature region (NTC) region.

Andrae *et al.* [32] studied the auto-ignition of primary reference fuels and toluene/*n*-heptane blends under HCCI conditions. They used an adiabatic single-zone model to simulate RCM and shock tube data and subsequently applied the detailed kinetic mechanism to model the HCCI experiment. RCM data experiments were conducted by Tanaka *et al.* [33] with flat piston heads. The agreement between simulated and experimental RCM data was poor. Andrae *et al*. documented that this discrepancy may be due to 'a *n*-heptane mechanism that is not perfectly tuned under these [HCCI] conditions', however, they failed to acknowledge the well known unsuitability of an adiabatic model to simulate RCM conditions. Westbrook et al. [34] addressed the problem of heat losses in the RCM by applying a Newtonian heat loss term at the cylinder surface, assuming that the temperature and fuel composition is uniform at any time. They estimated the heat loss by matching experimental and simulated pressure data for non-reactive gases and assigned two different heat loss coefficients, W, for the compression and post-compression periods. Their approach is a step forward from a homogeneous and averaged heat loss rate, however, it still fails to address spatial inhomogeneities.

In summary, there is no off-the-shelf simulation tool available that allows the realistic description of combustion in the RCM. Assumptions are required to reduce either the complex

environment to 1-dimensional descriptions, or alternatively, reduce the chemical kinetics in a complex environment. We believe that, until the computationally permissible liason of CFD and detailed chemistry is accomplished, the only viable solution is a 1-dimensional simulation including heat loss, for RCM data obtained exclusively with optimized piston head crevices.

Diluent Gases:

Diluent gases extend the range of compressed gas temperatures that can be reached in the RCM, while they help to achieve a well behaved shock wave in shock tubes. Because the compression ratio is fixed by the piston stroke in our RCM, the range of post-compression temperature and pressure for a given mixture composition is very limited. To overcome this constraint, the initial temperature is varied and different diluent gases are used which, based on their different thermal properties, will lead to largely different peak conditions. In our RCM the highest initial temperature is limited to ~125°C by the presence of PTFE and other seals, hence diluents with a low heat capacity, C_P, are required to reach high final temperatures. Typical diluent gases include helium, argon, nitrogen and carbon dioxide, however, we have advised previously not to use helium as a bath gas, due to its unfavorable thermo-physical properties, which cause an extreme loss of heat both during and after the compression stroke, thus rendering a kinetic simulation very difficult. In fact, based on a CFD study performed at our laboratory [8,9], we recommend xenon as an alternative because it reaches a high compressed gas temperatures and retains this for a longer time, due to its low heat capacity ratio, γ, and thermal conductivity of 5.192 mW m^{-1} K^{-1}.

It was assumed initially that the inert diluent gas has no direct effect on the experimental measurements in the shock tube or RCM. This study refutes this assumption below.

Heptane Isomers:

Experimental RCM data for all nine heptane isomers under stoichiometric conditions have been reported previously, at a compressed gas pressure of 15 atm and in the temperature range 600–960 K [35]. This was the first complete investigation of the nine isomers in the same study, although other studies have presented data for a number of the C_7 isomers in a small number of experimental devices [36,37]. Reliable data of this nature are essential in developing our understanding how fuel structure affects auto-ignition and combustion processes in kinetically controlled engine modes such as the homogeneous charge compression ignition engine, and to validate and refine chemical kinetic models of these processes. During our experimental RCM study of the isomers of heptane, a ‘diluent effect’ was observed, that is, a variation of the measured ignition delay time at the same compressed gas conditions for mixture containing different bath gases. Since it is standard practice to use a range of argon:nitrogen mixtures to extend the compressed gas conditions, some investigations were directed towards recording and quantifying this effect.

2. RCM Experimental

A number of heptane/oxygen/diluent mixtures were studied for which the proportions of two diluent gases, nitrogen and argon, were varied in order to alter the overall heat capacity of the mixture, thereby extending the range of compressed gas temperatures. All experiments were carried out

with creviced piston heads. Some physical properties of the diluent gases helium, argon and nitrogen are recorded in Table 1.

Table 1: Density, ρ, heat capacity, C_P, thermal conductivity (at 273 K), k, and thermal diffusivity of diluent, κ.

Species	ρ / kg m^{-3}	C_P / J K^{-1} mol^{-1}	k / J s^{-1} K^{-1} m^{-1}	κ / m^2 s^{-1}
He	0.179	20.786	0.1442	1.55e-4
Ar	1.783	20.786	0.0163	1.76e-5
N_2	1.251	29.125	0.0240	1.85e-5

The thermal conductivity, k, links the rate of heat loss, dQ/dt, per unit area, A, and the temperature gradient, ΔT:

$$(1/A)(dQ/dt) = -k\Delta T$$

It is not constant but increases with increasing temperature and can usually be fitted to a polynomial function of the type:

$$k = a + bT + cT^2$$

In addition to using two different diluent gases to extend the range of the final conditions, the initial gas temperature was varied with a thermostat fitted to the combustion chamber, as described previously [35]. For each of the nine isomers of heptane, three fuel and 'air' mixtures were investigated to cover the overall compressed gas temperature range of 600–950 K. The lowest temperatures were obtained using pure nitrogen as diluent (approximately 600–725 K), intermediate temperatures were achieved using a 50:50 mixtures of nitrogen and argon (700–825 K) and the highest temperatures were obtained using argon only (800–950 K). For 2,3-dimethylpentane (23DMP), an additional fuel in 'air' mixture of the ratio 0.75 N_2 / 0.25 Ar was examined and 3,3-dimethylpentane was studied in 0.25 N_2 / 0.75 Ar [35].

Due to the variations of diluent proportions and the use of the thermostat, some compressed gas temperatures overlapped for the three fuel/'air' mixtures, for which the only difference was the actual mixture diluent composition at the particular compressed gas temperature. For all heptanes under investigation, the ignition delay times, recorded at the same compressed gas temperature, were consistently longer when argon was used as the sole diluent, Fig. 1.

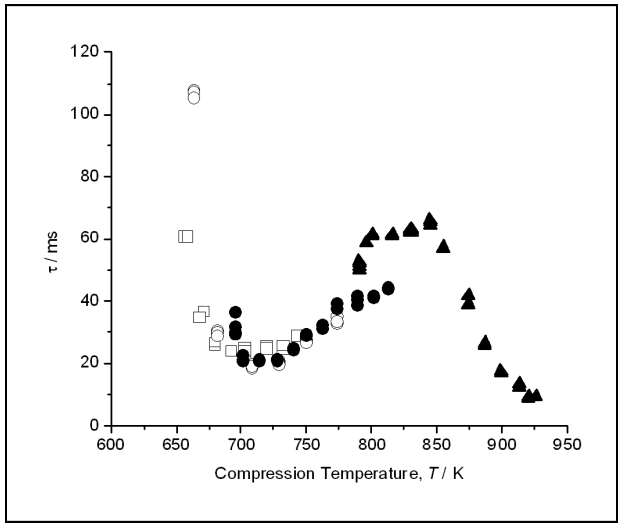

Figure 1: 23DMP, φ = 1.0, ~ 15 atm; Bath gas: □ N_2, ○ N_2:Ar=3:1, ● N_2:Ar=1:1, ▲ Ar.

For example, ignition delay times measured for 2,3-dimethylpentane at 800 K were 61 ms for pure argon and 41 ms for the 0.50 N_2 / 0.50 Ar diluent mixture. Ignition delay times recorded for the 0.75 N_2 / 0.25 Ar mixtures fitted neatly between the 0.50 N_2 / 0.50 Ar and pure argon mixtures. The elongation of ignition delay times in pure argon is apparent in the negative temperature coefficient (NTC) region only.

2.1 RCM Results and Discussion

Ar *versus* N_2

Some unusual results were recorded whereby the ignition delay times at the same compressed temperature and fuel and oxygen composition varied substantially for mixtures containing different fractions of nitrogen and argon diluent gases. The ignition delay times are directly related to the fraction of argon present, Table 2. This difference is due to the thermal properties of the diluent gases, such as the heat capacities, and/or the thermal diffusivities. Compression profiles for some typical pure diluent gases show the characteristic loss of pressure, particularly in the post-compression phase, Fig. 2.

Table 2: Ignition delay times with varying diluents at almost identical T_C, p_C ~ 15 atm.

Mixture	*T* / K	τ / ms
23DMP/O_2/N_2:Ar = 3:1	750	24.4
23DMP/O_2/N_2:Ar = 1:1	750	29.2
23DMP/O_2/N_2:Ar = 3:1	773	34.3
23DMP/O_2/N_2:Ar = 1:1	773	38.2

23DMP/O_2/N_2:Ar = 1:1	788	41.7
23DMP/O_2/N_2:Ar = 0:1	790	52.0
23DMP/O_2/N_2:Ar = 1:1	812	44.2
23DMP/O_2/N_2:Ar = 0:1	815	61.2

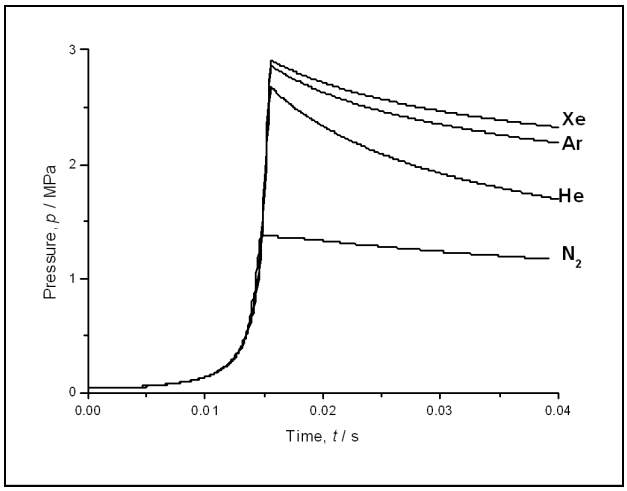

Figure 2: Experimental *p-t* profiles, typical diluent gases, flat piston head, T_i = 298 K, p_i = 0.040 MPa.

Not surprisingly, nitrogen reaches a much lower final pressure than helium, argon and xenon because of its high heat capacity. More importantly, the pressure loss in the post-compression period is most extreme for helium, followed by argon, due to their low heat capacity ratio (γ), and high thermal diffusivity. The large variation in ignition delay times that were recorded for mixtures of heptanes with varying proportions of argon and nitrogen is caused by the difference in post-compression pressure and temperature loss; mixtures with nitrogen will maintain a higher temperature for longer than an otherwise identical mixture with argon diluent. Hence, τ for the argon mixture will be 'stretched out' at the same compressed gas temperature. Thus, it was concluded that there is no single smooth τ vs. T curve for a fuel when different diluent gases are used to extend the temperature range. Ignition delay time becomes a function of the characteristic heat loss of the mixture composition.

In order to investigate this diluent effect in more detail, some additional experiments were performed with 2,3-dimethylpentane in both pure argon and helium. Argon and helium have identical heat capacities, but different thermal conductivities, with $k_{He} > k_{Ar}$, Table 1. The following was observed:

- The compressed pressure of the helium mixture was always lower than that obtained with the corresponding argon counterpart, Fig. 3.
- The ignition delay times measured for the helium mixture were much longer than those recorded for the argon mixture — for example He ~80 ms compared to Ar ~25.5 ms at T_C = 890 K, Fig. 4.

Analogous to the unreactive compression profiles, it was observed that the final pressure reached by the helium mixture was lower than that measured with argon, caused by higher heat losses during the compression stroke, Fig. 3.

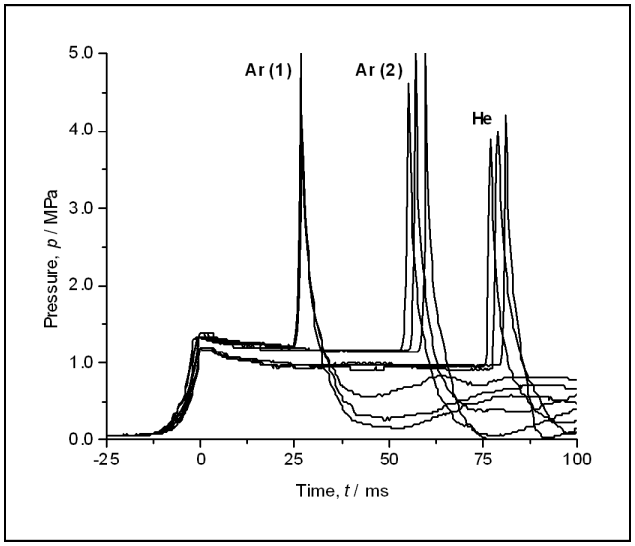

Figure 3: 23DMP in Ar *vs.* in He, φ = 1.0, ~ 15 atm, Ar (1) T_i = 335 K, Ar (2) T_C = 854 K, He T_i = 335 K and T_C = 854 K.

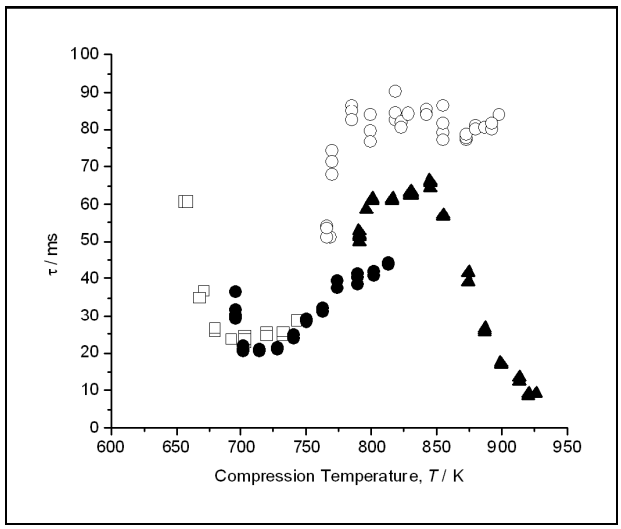

Figure 4: 23DMP, φ = 1.0, ~ 15 atm; Bath gas: □ N_2, ● N_2:Ar=1:1, ▲ Ar, ○ He.

Due to this difference in the final pressure and thus temperature, the above experiments were repeated at an equal compressed gas temperature, T_C, of 854 K, Ar(2) in Fig. 3. The measured ignition delay times differed by 23 ms, with τ_{He} = 80 ms and τ_{Ar} = 57 ms - the difference stemming from the higher thermal conductivity of helium. Helium has the ability to carry heat to

the chamber walls at a much faster rate, thus cooling faster and elongating τ as a result. The observed difference is substantial, leading us to the conclusion, in support of our previous findings [8], not to use helium as bath gas for rapid compression machine experiments.

2.2 Simulating heat loss in the RCM:

There is currently no simulation tool available that would allow a realistic description of the RCM environment. The assumption of adiabatic conditions in a 1–dimensional model is unacceptable: due to the long test times involved, heat losses play an important role in the RCM experiment, as shown particularly for the set of experiments investigated in this study. In an effort to reproduce and quantify the diluent-specific elongation of ignition delay time for mixtures containing higher proportions of argon, time pressure profiles were simulated for pure argon and pure nitrogen, and their intermediate mixtures in various compositions (10:90, 25:75, 50:50, 75:25, 100:0) using HCT [38] and Chemkin [39]. The heat loss profiles that were generated by matching experimental traces of pressure were then applied to auto-ignition simulations of 23DMP.

HCT implements heat losses through a Newtonian heat loss term at the surface, assuming a uniform temperature, *T*, and composition at any given time, *t*. The heat loss to the wall, *W* is approximated by a term in the energy equation [38]:

$$dt/t = -W[T - T(\text{wall})]$$

In this study heat loss coefficients were generated for pure argon and nitrogen by matching experimental pressure profiles obtained at identical initial conditions. The heat loss coefficients for intermediate argon and nitrogen mixtures were subsequently averaged from the pure gas traces and included through the key word 'wall'. Due to the shape of the experimental pressure traces, the simulations were performed in three separate sections (0–14.6 ms (the time for compression); 14.6–38 ms (the time immediately after compression); and 38–200 ms). The heat loss coefficients of the compression and final sections were matched, while that of the intermediate section was assigned a higher value to account for the more drastic pressure loss during this time.

The predicted pressure profiles for the intermediate argon-nitrogen mixtures were in good agreement with the experimental traces, Figs. 5–6. The largest discrepancies are seen for mixtures containing higher proportions of argon, which are, of course, characterized by much higher compressed gas temperatures, which are not accounted for in this method of simulation. The application of the generated heat loss coefficients to the simulation of ignition delay time of 23DMP was not successful. Matching the inert pressure traces as outlined above, and transferring the heat loss profiles for each argon/nitrogen composition to simulations of 23DMP which were diluted in the same composition of argon/nitrogen was not sufficient to reproduce the elongating effect that were seen in the experiment.

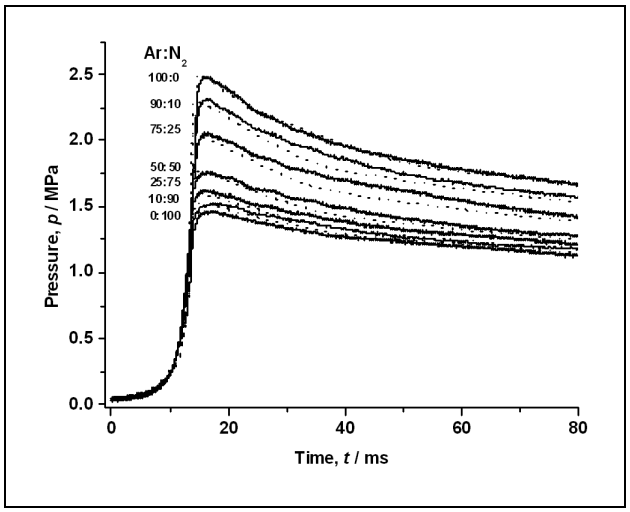

Figure 5: Pressure profiles (T_i = 298 K, p_i = 0.050 MPa), solid: experiment, dotted: CHEMKIN with QPRO function.

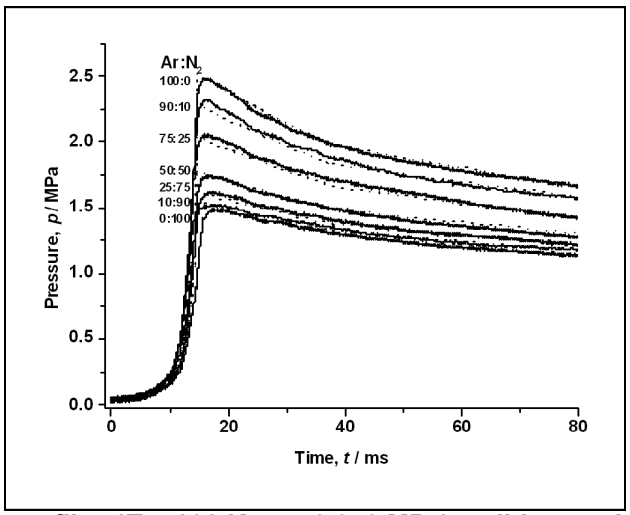

Figure 6: Pressure profiles (T_i = 298 K, p_i = 0.050 MPa), solid: experiment, dotted: HCT.

3. Shock Tube

Shock tube experiments are generally carried out with a premixed mixture of fuel, oxygen and argon, since the shock wave behavior is optimized in a monatomic carrier gas. The use of monatomic carrier gas eliminates the influence of vibrational relaxation in the carrier gas, as well as eliminating or minimizing shock wave bifurcation near the wall in the reflected shock front [19]. Dilute fuel mixtures with large proportions of argon are therefore studied at more optimal conditions than more concentrated mixtures, for which the fraction of polyatomic gas would be much higher.

3.1 *Iso*-octane:

Davidson *et al.* recently evaluated shock tube ignition delay time data in terms of both type and quality for developing and validating combustion reaction mechanisms. They included an evaluation of the effect of diluent gas on the ignition delay time, for an *iso*-octane/oxygen/diluent mixture based on two kinetic mechanisms. Davidson *et al*. predicted, based upon the Davis and Law detailed mechanism [20], an increase in the ignition delay time by 9 ms if the diluent argon was replaced by nitrogen for a mixture containing 0.16% *iso*-octane, 2% oxygen and 97.84% diluent gas.

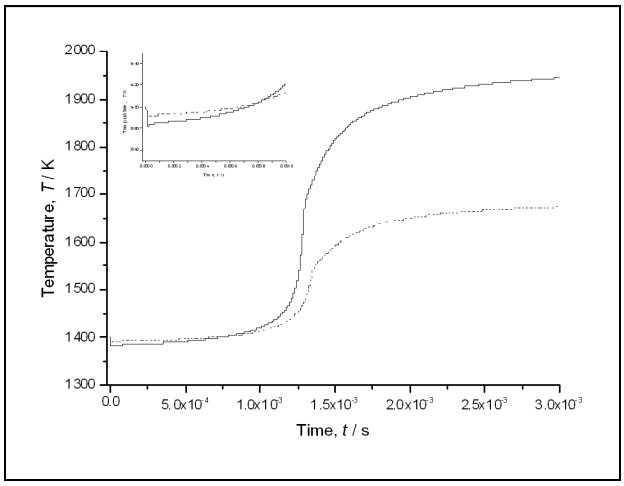

Figure 7: Temperature profiles: 0.16% *i*-C_8H_{18}, 2% O_2, 97.84% diluent at 2 atm and 1,400 K - - - N_2, — Ar.

Calculations were repeated for *iso*-octane in 'air' which confirm the findings by Davidson *et al.* For the dilute mixture we made the following observations, Fig. 7:

- During the initial phase, whilst pyrolytic decomposition of the fuel takes place, the endothermic reactions cause the temperature of the mixture to fall — this fall is more pronounced for argon because of its inability to store energy in any modes other than its translational degrees of freedom (C_V = 3*RT*/2). By contrast, the temperature of the nitrogen mixture does not fall as far because of its additional rotational degrees of freedom of the nitrogen molecule (C_V = 5*RT*/2).
- Once the radical pool begins to build, the exothermicity of this phase causes the argon temperature to rise faster than that of the nitrogen mixture and eventually overtakes it - in this case at about 700 μs.
- In the final - highly exothermic - phase, the temperature of the argon mixture rises earlier than that of the nitrogen mixture and accelerates the ignition.

In contrast when the amount of the diluent is decreased to 73.53%, Fig. 8, the difference in τ between the mixtures containing argon and nitrogen is now much smaller, circa 1%, although the overall behavior is similar to that previously described. Note that the T–t profiles for argon and nitrogen are very close, particularly as regards the final temperature rise. In practical terms, mixtures of this composition are not a good choice for shock tube work because of non-ideal effects resulting from the use of a diatomic gas as a diluent [40]. Both the simulations by Davidson *et al.* and those of this study are only modeling predictions and, as a result, must be interpreted with caution. The approach may be flawed because:

1. There are no experiments to support these results
2. N_2 chemistry was not included in either study

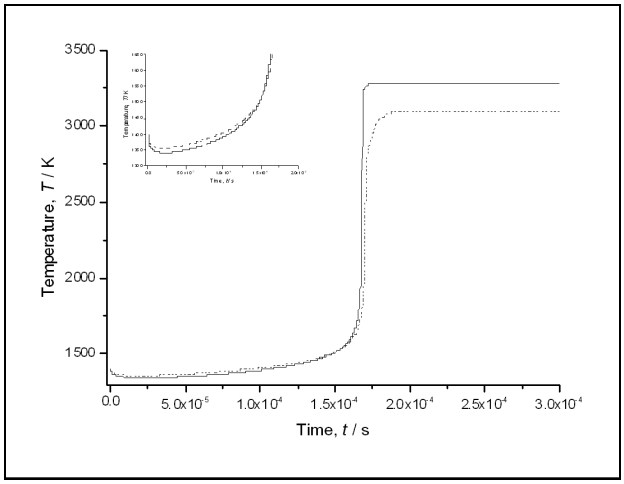

Figure 8: Temperature profiles: 1.96% *i*-C_8H_{18}, 24.51% O_2, 73.53% diluent at 2 atm and 1,400 K - - - N_2, — Ar.

3.2 Methane

We simulated methane ignition in the HCT modeling code [38], for both dilute and concentrated mixtures at T = 1500 K and T = 1800 K, Figs. 9–12. There was no significant difference in the predicted behaviour for the dilute and concentrated methane mixtures: contrary to *iso*-octane, the methane–argon mixture was consistently faster, regardless of the degree of dilution, Table 3.

Table 3: HCT predicted ignition delay times.

Temperature / K	τ_{Ar} / μs	τ_{N2} / μs
1500	7517	8357
1800	346.7	340.3

Table 4: Synopsis of main consumption paths for methyl radical at 10% fuel consumed.

	Ar	N_2
% fuel consumed	9.67	9.45
T / K	1510.4	1505.0
Time / μs	5205	5007
Rate of CH_3 consumption / mol cm^{-3} s^{-1}	5.39e-6	4.77e-6
Contribution to CH3 consumption		
$CH_3 + CH_3 + M = C_2H_6 + M$	31.9%	32.4%

$CH_3 + O_2 = CH_2O + OH$	28.4%	28.7%
$CH_3 + CH_2O = HCO + CH_4$	20.3%	20.1%
$CH_3 + C_2H_6 = C_2H_5 + CH_4$	9.1%	9.25%
$CH_3 + CH_3 = C_2H_5 + H$	6.0%	5.5%
$CH_3 + C_2H_4 = C_2H_3 + CH_4$	4.2%	4.1%

In order to investigate more fully why ignition delay times are faster in Ar relative to N_2 diluent we performed a rate of production analysis under dilute conditions: 0.91% CH_4, 1.81% O_2, 97.28% Ar/N_2, T_i = 1500 K, p_i = 1.8 atm. We found that any CH_4 that is oxidized becomes methyl radical. Thus, the fate of CH_3 radicals has been studied. Tables 4–7 show the most important reactions consuming and producing methyl radicals at approximately 10% fuel consumption, Table 4, 20% consumption Table 5, 30% consumption, Table 6, and 40% consumption, Table 7.

Table 5: Synopsis of main consumption paths for methyl radical at 20% fuel consumed.

	Ar	**N_2**
% fuel consumed	21.9	20.6
T / K	1525.3	1511.8
Time / μs	6405	6607
Rate of CH_3 consumption / mol cm^{-3} s^{-1}	1.70e-5	1.19e-5
Contribution to CH3 consumption		
$CH_3 + CH_3 + M = C_2H_6 + M$	29.9%	32.6%
$CH_3 + O_2 = CH_2O + OH$	14.9%	16.8%
$CH_3 + CH_2O = HCO + CH_4$	12.0%	13.2%
$CH_3 + O = CH_2O + H$	9.0%	8.0%
$CH_3 + C_2H_6 = C_2H_5 + CH_4$	8.9%	9.7%
$CH_3 + C_2H_4 = C_2H_3 + CH_4$	7.2%	7.4%
$CH_3 + HO_2 = CH_3O + OH$	6.7%	7.2%
$CH_3 + OH = CH_2(s) + H_2O$	6.1%	-
$CH_3 + CH_3 = C_2H_5 + H$	5.4%	5.0%

Analysis of these results indicates that $CH_3 + CH_3 + M = C_2H_6 + M$ is always slightly more important in the case of N_2 diluent relative to Ar diluent. This was further analyzed by changing the third body efficiency for Ar from 0.7 to 1.0, to equal that for N_2. In this case for Ar diluent at 1500 K the ignition delay time changed from 7517 μs to 7810 μs, and at 1800 K the ignition delay time changed from 346.7 μs to 349.5 μs. Thus, the third body efficiency of Ar is making the ignition delay time slightly longer and so the relative efficiency factors of Ar and N_2 are contributing to the longer ignition delay times for N_2 relative to Ar.

Table 6: Synopsis of main consumption paths for methyl radical at 30% fuel consumed.

	Ar	N_2
% fuel consumed	21.9	28.4
T / K	1534.9	1517.0
Time / μs	6805	7207
Rate of CH_3 consumption / mol cm^{-3} s^{-1}	2.74e-5	1.95e-5
Contribution to CH3 consumption		
$CH_3 + CH_3 + M = C_2H_6 + M$	30.4%	32.4%
$CH_3 + O = CH_2O + H$	12.0%	10.2%
$CH_3 + O_2 = CH_2O + OH$	11.5%	12.3%
$CH_3 + CH_2O = HCO + CH_4$	9.6%	9.8%
$CH_3 + C_2H_4 = C_2H_3 + CH_4$	8.2%	8.4%
$CH_3 + C_2H_6 = C_2H_5 + CH_4$	8.1%	8.6%
$CH_3 + OH = CH_2(s) + H_2O$	8.0%	6.8%
$CH_3 + HO_2 = CH_3O + OH$	6.8%	7.0%
$CH_3 + CH_3 = C_2H_5 + H$	5.4%	4.6%

To explore this further, all reactions in which third bodies play a role were modified such that the efficiency for Ar was forced to 1.0 (the efficiency for N_2 in all reactions) resulting in the following ignition delay times: at 1500 K the time went from 7517 μs to 7712 μs and at 1800 K the predicted time went from 346.7 μs to 326.4 μs, Table 8. This shows that, with all efficiencies are the same, the ignition delay time predicted at 1500 K for Ar diluent is slightly longer than that predicted for Ar originally but is still significantly faster than with N_2 diluent. At 1800 K the picture is even clearer; changing the efficiencies associated with Ar leads to a faster ignition delay time than with Ar originally and the prediction is always faster than with N_2 as diluent. Thus, it is not the efficiencies of Ar relative to N_2 diluent that are responsible for longer ignition delay times in N_2 diluent. Thus, we conclude that this behavior is associated with the heat capacity of bath gas. Nitrogen with its higher heat capacity take more heat out of the system relative to argon diluent resulting in longer ignition delay times, particularly at lower temperatures. It should be noted also in Tables 4–7 that the total rate of CH_3 radical consumption is always greater in Ar diluent than in N_2 diluent. We believe this to be due to a higher overall rate of reaction at higher temperature.

We repeated the same simulation for dilute and concentrated methane mixtures at a temperature of 1800 K, Figs. 11–12. At this temperature the diluent effect is less pronounced. The difference in the low and high temperature chemistry is responsible for the variation in the diluent effect: at low temperatures, the hydrogen abstraction reaction $CH_4 + OH \rightarrow CH_3 + H_2O$ dominates the attack on the fuel molecule. This exothermic reaction results in the mixtures containing higher proportions of argon to heat up faster than those made up with nitrogen, due to the much lower heat capacity of argon. This earlier and more intense increase of temperature then gives rise to faster ignition. However, at high temperatures, the initiation is dominated by the endothermic

reaction $CH_4 \rightarrow CH_3 + H$, followed by $H + O_2 \rightarrow O + OH$. The initial unimolecular decomposition causes the mixtures containing high proportions of argon to loose more heat. This is followed by the exothermic chain branching reaction of H with molecular oxygen. The overall effect is a balancing of the two reactions, resulting in very similar ignition delay times for mixtures with argon and nitrogen.

Table 7: Synopsis of main consumption paths for methyl radical at 40% fuel consumed.

	Ar	**N_2**
% fuel consumed	43.4	42.5
T / K	1556.1	1527.6
Time / μs	7205	7807
Rate of CH_3 consumption / mol cm^{-3} s^{-1}	6.60e-5	4.13e-5
Contribution to CH3 consumption		
$CH_3 + CH_3 + M = C_2H_6 + M$	28.7%	32.9%
$CH_3 + O = CH_2O + H$	19.3%	16.0%
$CH_3 + OH = CH_2(s) + H_2O$	13.2%	10.8%
$CH_3 + C_2H_4 = C_2H_3 + CH_4$	8.2%	8.7%
$CH_3 + O_2 = CH_2O + OH$	6.9%	7.7%
$CH_3 + HO_2 = CH_3O + OH$	6.8%	7.0%
$CH_3 + CH_2O = HCO + CH_4$	6.3%	6.3%
$CH_3 + C_2H_6 = C_2H_5 + CH_4$	5.7%	6.3%
$CH_3 + CH_3 = C_2H_5 + H$	5.1%	4.2%

Table 8: HCT predicted ignition delay times.

Temperature / K	**Ignition delay time / μs**			
	Ar	**N_2**	**C_2H_6 + M**	**All Ar → 1.0**
1500	7517	8357	7801	7712
1800	346.7	340.3	349.5	326.4

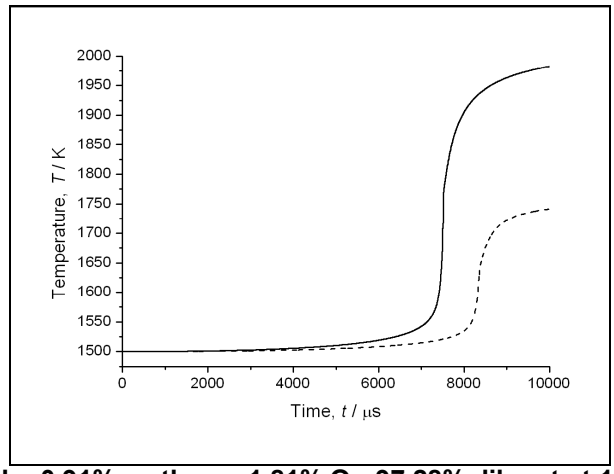

Figure 9: *T*- *t* profile: 0.91% methane, 1.81% O_2, 97.28% diluent at 1.8 atm and 1,500 K - - - N_2, — Ar.

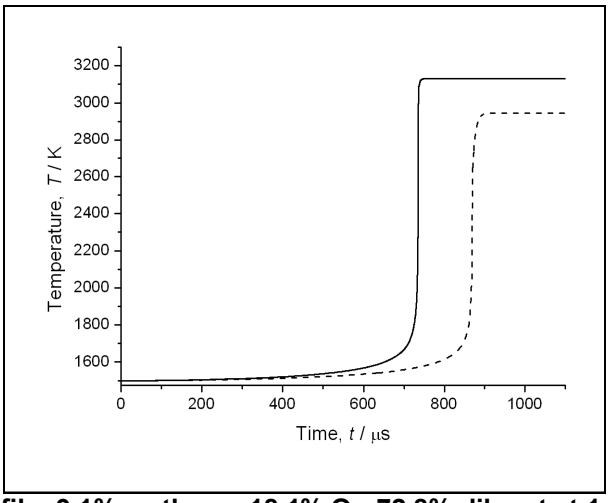

Figure 10: *T*- *t* profile: 9.1% methane, 18.1% O_2, 72.8% diluent at 1.8 atm and 1,500 K - - - N_2, — Ar.

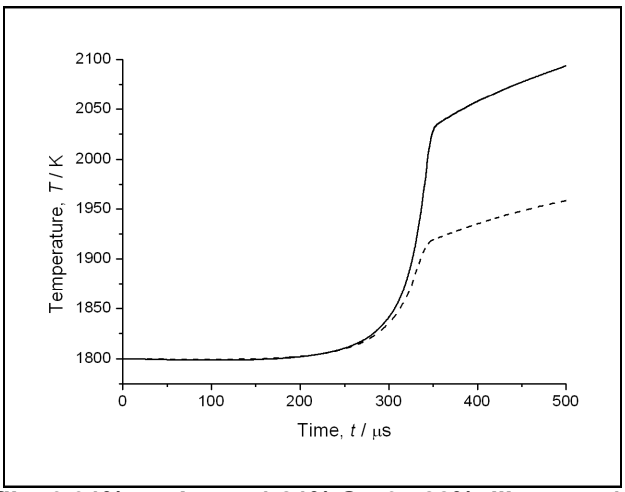

Figure 11: *T*- *t* profile: 0.91% methane, 1.81% O_2, 97.28% diluent at 1.8 atm and 1,800 K - - - N_2, — Ar.

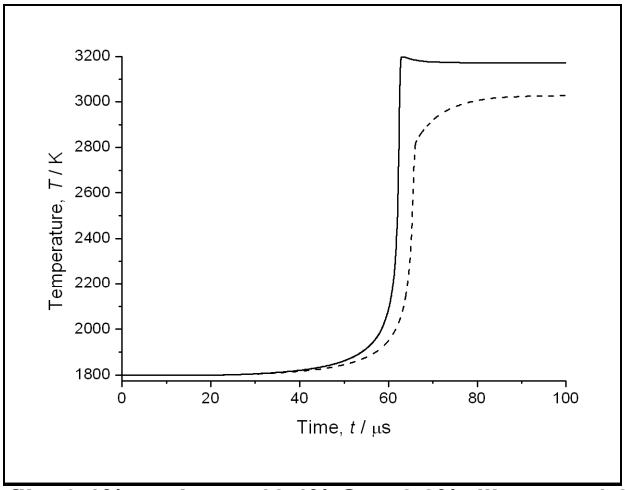

Figure 12: *T*- *t* profile: 9.1% methane, 18.1% O_2, 72.8% diluent at 1.8 atm and 1,800 K - - - N_2, — Ar.

4. Conclusion

Diluent gases extend the range of temperatures that can be reached for a particular gas mixture in the RCM, while monatomic argon is used to optimize the shock conditions in the shock tube. The diluent gas is inert and does not take part in the chemical reaction, however, it does have an effect on the measured ignition delay time in both experimental devices — argon decelerates ignition in the RCM, but accelerates it in the shock tube under some conditions.

This opposite effect is due to the times scales involved in these experimental devices. Typical ignition delay times in the RCM are in the region of 1−200 ms, while that of the shock tube are much shorter (10−1,000 μs). Comparative RCM experiments and simulations for helium, argon, xenon and nitrogen have shown extreme heat loss in the post-compression period, in particular for helium. Auto-ignition measurements of 23DMP have highlighted a direct dependency of τ with the type of diluent used, where longer ignition delay time were recorded with argon. Experimental results have shown a difference in _ for 23DMP of 38% when the diluent was changed from pure argon to a 50:50 mixture of argon and nitrogen. This increased ignition delay time is due to the extreme cooling of argon in the post-compression period. This observation was strengthened by comparative experiments with helium and argon, where the diluent effect was even stronger for helium caused by its higher thermal conductivity.

In the shock tube, the diluent effect is opposite to that in the RCM. For dilute mixtures of *iso*-octane, calculations have predicted that mixtures with argon will ignite before those with nitrogen, based on the low heat capacity of argon. However, this effect becomes much weaker for concentrated mixtures of *iso*-octane, in which the diluent content is reduced to 74%, and the heat capacity of the mixture is raised by the larger proportions of multi-atomic oxygen and fuel. In the case of methane, predictions showed little difference in the behavior of dilute and concentrated mixtures, however, the diluent effect was shown to disappear at higher temperatures. This was explained based on the chemistry that dominates the reactive systems at the two temperature regimes. Overall, we concluded that the choice of diluent gases in

experimental devices must be made with care as τ can depend strongly on the type diluent gas under certain conditions.

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References

[1] Park, P. and Keck, J. C., Soc. Auto. Eng. Paper(900027): pp.11–23(1990).
[2] Affleck, W.S., Thomas, A., Proc. Inst. Mech Eng., Vol. 183, pp.365–385 (1968).
[3] Lee, D. and Hochgreb, S. Combust. Flame, Vol. 114, pp. 531–545 (1998).
[4] Clarkson, J., Griffiths, J. F., Mac Namara, J. P. and Whitaker, B. J., Combust. Flame, Vol. 125(3), pp. 1162–1175 (2001).
[5] Griffiths, J. F., Jiao, Q., Schreiber, M., Meyer, J. and Knoche K. F., Proc. Combust. Inst., Vol. 24, pp. 1809–1815 (1992).
[6] Griffiths, J. F., MacNamara, J. P., Mohamed, C., Whitaker, B. J., Pan, J. F. and Sheppard, C. G. W., Faraday Discussions, Vol. 119, pp.287–303 (2001).
[7] Donovan, M. T., He, X., Zigler, B. T., Palmer, T. R., Wooldridge, M. S. and Atreya, A., Combust. Flame, Vol 137(3), pp. 351–365 (2004).
[8] Würmel, J., Ph.D. Thesis, National University of Ireland, Galway (2004).
[9] Würmel, J. and Simmie, J. M., Combust. Flame, Vol. 141(4), pp. 417–430 (2005).
[10] Mittal, G., Sung, C.-J., 30th Int. Symp. on Combustion 4F1–17, WIP poster (2004).
[11] Mittal, G. and C.-J. Sung, Combust. Flame, Vol. 145(1-2), pp.160–180 (2006).
[12] http://powerlab.mech.okayama-u.ac.jp/~esd/comodia2004/C6_1_049.pdf
[13] Iida, M., Hayashi, M., Foster, D. E. and Martin, J. K., ASME, Vol. 125, pp. 472–478 (2003).
[14] Dagaut, P., Luche, J. and Cathonnet, M., Energy & Fuels, Vol. 14, pp. 712–719 (2000).
[15] Held, T. J., Dissertation thesis, Princeton University (1993).
[16] Herzberg, A., Smith, W., Glick, H. S. and Squire, W. M., Reports AD-789-A-2, AEDC-TN- 55-15, Cornell Aerodynamics Lab, Buffalo, New York (1955).
[17] Amadio, A., Petersen, E. L. and Crofton, M. W., 25th Int. Symposium Shock Waves, paper 1280 2a, Bangalore (2005).
[18] Shock: A general Pupose computer code for predicting chemical kinetic behaviour behind incident and reflected shocks. (2004) R. J., Rupley, F. M., Miller, J. A., Coltrin, M. E., Grcar, J. F., Meeks, E., Moffat, H. K., Lutz, A. E., Dixon-Lewis, G., Smooke, M. D., Warnatz, J., Evans, G. H., Larson, R. S., Mitchell, R. E., Petzold, L. R., Reynolds, W. C., Caracotsios, M., Stewart, W. E., Glarborg, P., Wang, C., Adigun, O., Houf, W. G., Chou, C. P., Miller, S. F., Ho, P., Young, D. J., Chemkin Collection, Release 4, Reaction Design, Inc., San Diego, CA.
[19] Davidson, D. F. and Hanson, R. K., Int. J. Chem. Kinet. 36:510–523 (2004).
[20] Davis, S.G. Law, C. K., Proc. Combust. Inst., 27, 521–527 (1998).
[21] Pitsch, H., Peters, N., Seshadri, K., Proc. Combust. Inst. 26:763–771 (1998).
[22] Chien, X. J., Wakai, K., Takahashi, S., Ihara, T. and Shibata, K., Measurement Science & Technology, Vol. 16 pp. 707–715 (2005).
[23] Griffiths, J. F. and Whitaker, B. J., Combust. Flame, Vol. 131, pp. 386–399 (2002).
[24] Orme, J. P., Ph.D. thesis, National University of Ireland, Galway (2005).
[25] Minetti, R., Ribaucour, M., Carlier, M., Fittschen, C. and Sochet, L. R., Combust. Flame 96:102–211 (1994).
[26] Van Blarigan, Proc. 1999 U.S. DOE Hydrogen Program review NREL/CP-570-26938 (1999).
[27] http://ci.confex.com/ci/2005/techprogram/P1944.HTM
[28] Brett, L., Ph. D.thesis, National University of Ireland, Galway (1999).
[29] Benkenida, A. and Angelberger, C., Combust. Sci. and Tech., Vol. 176, pp. 667–68 (2004).

[30] Shi, S., Lee, D. McSurdy, S., McMillian, M., Richardson, S. and Rogers, W., Int. Comb. Eng. Div. of ASME Fall technical Conference (2002).
[31] Ribaucour, M., Lemaire, O. and Minetti, R., Proc. Combust. Inst., (29) pp. 1303–1310 (2002).
[32] Andrae, J., Johanssona, D., Bjrnboma, P., Risbergb, P and Kalghatgi, G., Combust. Flame, Vol. 140, pp. 267–286 (2005).
[33] Tanaka, S., Ayala, F. Keck, J.C. and Heywood, J.B., Combust. Flame, Vol. 132, pp.219–239 (2003).
[34] Westbrook, C. K., Pitz, W. J., Curran, H. J., Boercker, J., Griffiths, J. F., Mohamed C., and Ribaucour, M., Proc. Combust. Inst. 29:1311–1318 (2002).
[35] Silke, E. J., Curran H. J. and Simmie, J. M. Proc. Combust. Inst. 30:2639–2647 (2005).
[36] Griffiths, J. F., Halford-Maw, P. A., and Mohamed, C., Combust. Flame 111:327–337 (1997).
[37] McEnally, C. S., Ciuparu, D. M., Pfefferle, L. D., Combust. Flame 134:339–353 (2003).
[38] Lund, C.M., Lawrence Livermore National Laboratory report, ucrl–52504 (1978).
[39] CHEMKIN 2004 Kee, (2004) R. J., Rupley, F. M., Miller, J. A., Coltrin, M. E., Grcar, J. F., Meeks, E., Moffat, H. K., Lutz, A. E., Dixon-Lewis, G., Smooke, M. D., Warnatz, J., Evans, G. H., Larson, R. S., Mitchell, R. E., Petzold, L. R., Reynolds, W. C., Caracotsios, M., Stewart, W. E., Glarborg, P., Wang, C., Adigun, O., Houf, W. G., Chou, C. P., Miller, S. F., Ho, P., Young, D. J., Chemkin Collection, Release 4, Reaction Design, Inc., San Diego, CA.
[40] Greene, E. F., Toennies, J. P., Chemical reactions in shock waves, Edward Arnold, London, 1964, p. 140.
[41] Smith, G. P., Golden, D. M., Frenklach, M., Moriarty, N. W., Eiteneer, B., Goldenberg, M., C.T. Bowman, Hanson, R. K., Song, S., Gardiner, Jr., W., Vitali V., Lissianski, C. and Qin, Z., http://www.me.berkeley.edu/gri_mech/